Conference Highlights

ICONN 2006: The 2006 International Conference on Nanoscience and Nanotechnology, Brisbane, Australia, July 2006

Over four hundred delegates attended the Brisbane conference with a strong overseas component. Element 79 cropped up in some form in nearly a fifth of the papers or presentations. Its appearance at the conference could be broadly grouped into two main themes – gold as a conductive substrate on which to assemble organic molecules, and gold as a conduit or resonator for surface plasmons. There was also a 'grab bag' of other aspects involving gold.

Much of the interest in the first theme is driven by an interest in so-called 'molecular electronics', a notional scheme in which the transistors, diodes, capacitors and interconnects of traditional silicon-based integrated circuitry would be replaced by nanoscale devices built up out of individual organic molecules. Enormous increases in circuit density can be imagined if the scheme could be realised. Of course, electric current must be brought up to the molecules which must also necessarily be attached to a suitable substrate, and gold is almost universally used in this field for both purposes. Mark Reed of Yale University (USA) summarised much of the current state-of-the-art in a keynote talk, while Rainer Hoft (University of Technology Sydney (UTS), Australia), Jan Hermann (CSIRO, Australia), and Colin Lambert (Lancaster Univ, UK) provided interesting talks on the theoretical and experimental aspects of this quest. In all cases the systems they studied were based on gold electrodes.

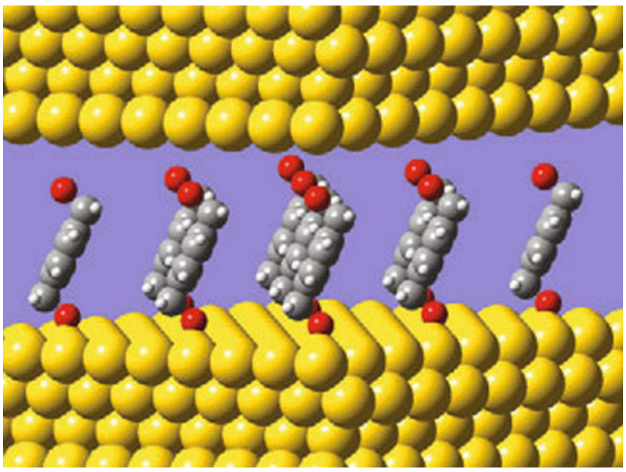

Figure 1
Schematic illustration of a molecular electronics junction, in which a layer of functional organic molecules is sandwiched between two gold electrodes (graphic courtesy of Rainer Hoft, Australia)

However, there are other, more immediate reasons than molecular electronics to attach organic molecules to gold. Alessia Mortari (Lund University, Sweden & UTS, Australia) described how very sensitive capacitive biosensors can be realised by attaching proteins that selectively bind to particular metal ions onto gold substrates, while Minoo Moghaddam (CSIRO, Australia) showed how gold nanoparticles and DNA can be attached to carbon nanotubes. In this case the idea is to develop a faradaic electrochemical sensor. Actually, it is even convenient to attach the carbon nanotubes themselves to gold contacts, and this possibility formed the basis of a poster by B.S. Flavel and colleagues (Flinders University, Australia). The general issues involved when attaching organic molecules to Au were addressed by Mike Ford (UTS, Australia) who proposed that alkynyl-based self-assembled monolayers would be worth investigating as possible alternatives to thiol-based ones, while his colleague Hadi Zareie described some state-of-the-art schemes to assemble functional monolayers onto gold substrates. Mike Cortie gave a talk on mesoporous gold sponges, and showed how these can serve as the electrodes for capacitive sensors, in this case for the proteinaceous absorption that occurs from milk.

Turning to the second theme, it is of course old news that gold and its nanoparticles display interesting optical properties in the visible and near-infrared regions of the spectrum. This fact has been exploited since Roman times but continues to be a very actively researched topic. This current interest is very much driven by 21st century needs. For example, Peter Zijlstra (Swinburne University of Technology, Australia) described their work on using gold nanorods in memory storage devices. When illuminated by a suitable laser source, the rods are irreversibly changed to spherical form with a large change in optical properties. This system is believed by Zijlstra and many others to offer the

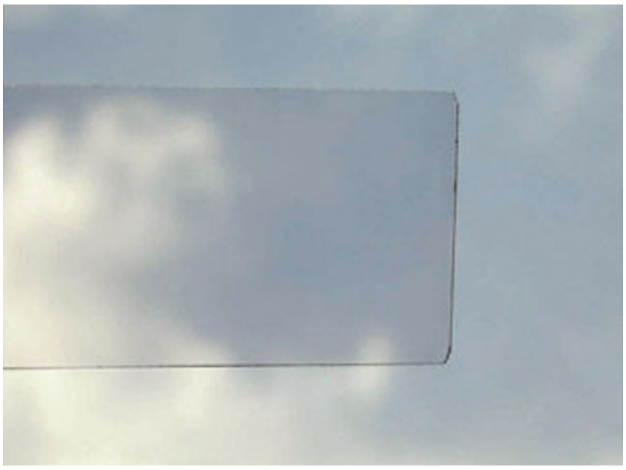

Figure 2
A collaborative project by UTS and AngloGold Ashanti has shown how coatings of gold nanoparticles can be deposited by wet chemical means onto glass for possible architectural use. By careful control of their interparticle spacing, a neutral or grey-blue tone can be obtained. These coatings have reasonable solar screening attributes and would cost about $US2 per m^2 to apply (photo courtesy of Institute for Nanoscale Technology, Australia)

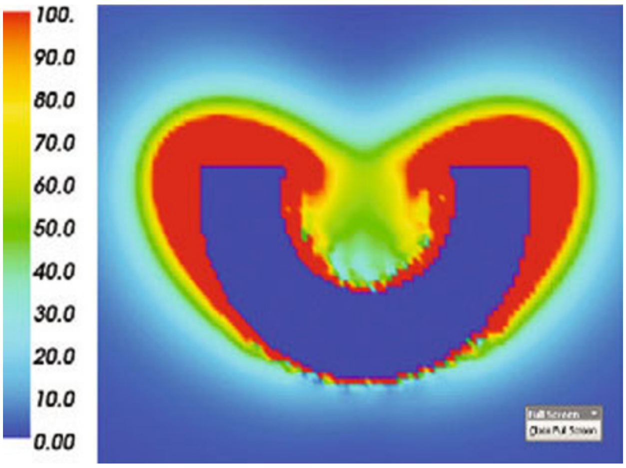

Figure 3

Intense electric fields developed around the rims of gold 'nano-caps' (seen here in cross-section) when they are illuminated by light at the dipole plasmon resonance frequency (courtesy of Burak Cankurtaran, Curtin University, Australia)

potential for a very stable, long-life system for DVD-like data storage. Xiaoda Xu (UTS, Australia) described how the optical absorption of coatings of gold nanoparticles on glass can be tuned so that they selectively attenuate the near-infrared while transmitting the visible. His colleague, Nadine Harris, in turn showed how there is a single, optimum geometry of gold nanoshell that provides maximum efficiency in respect of the conversion of light to heat. This operation, also termed 'plasmonic heating', is of great interest for potential photothermal medical therapies based on gold particles of diverse shapes.

There were also a brace of optically-oriented papers somewhat upstream of the application area. Carolina Novo (Univ. of Melbourne, Australia) showed elegant measurements of the optical properties of individual gold nanorods. Although these are far too small to be actually resolved in an optical microscope, the light that they scatter can be seen and hence fed into a spectrometer. In a slightly different vein, Mike Cortie presented work describing how

Figure 4

The unique plasmon resonance of gold nanoparticles can be used to colour glass, such as in these beautiful Victorian 'ruby' (left) and 'cranberry' (right) vases (courtesy of Mark Crittle, Thirroul Antiques, Australia)

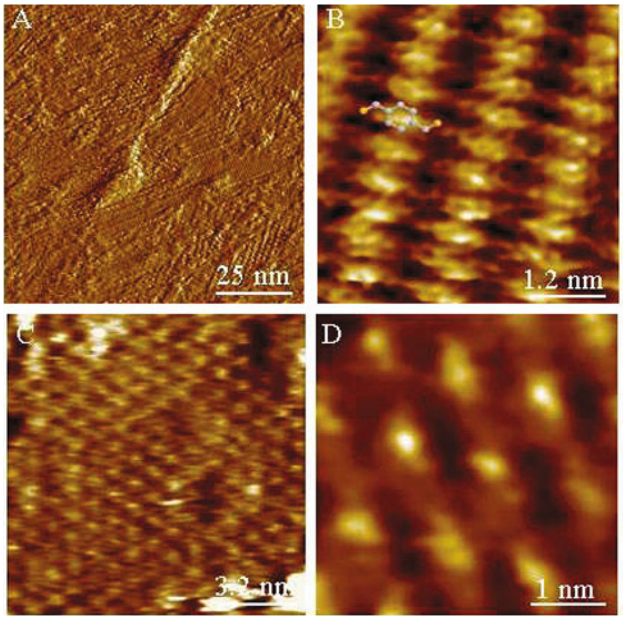

Figure 5

Ultra-high resolution images showing arrays of individual molecules of 1,4-phenylenedimethanethiol assembled onto a gold surface (images courtesy of Dr Hadi Zareie, Australia)

the optical properties of coatings formed by packing rods together will be influenced by the nature of the packing geometry. The effect can be harnessed and exploited to provide coatings of higher optical density. Finally, Burak Cankurtaran, and other colleagues, showed how cap-shaped gold nanoparticles could be arrayed to produce optically anisotropic coatings. These coatings behave somewhat like nanoscale 'venetian blinds'.

Of course the useful optical and chemical properties of gold can be exploited simultaneously. For example Chris Barton (CSIRO, Australia) showed how gold nanospheres can be coated with histidine-tagged proteins and then used in principle in a colorimetric assay for G-proteins, while Matthew Nussio *et al.* (Flinders University, Australia) used Surface Plasmon Resonance (carried out of course on a gold substrate) to study protein-membrane interactions, and Tara Schiller, Zul Merican and other colleagues (Queensland University of Technology & University of Queensland, Australia) described how hybrid gold-polymer particles could be exploited to make ultrasensitive Surface Enhanced Raman measurements. This latter theme was also the focus of Kym Watling (Griffith University, Australia) who showed how dendritic electrodeposits of gold provided a useful substrate for SERS. In a related vein, Fang Xie and Ewa Goldys (Maquarie University, Australia) presented a poster on the use of Au/Ag composite particles to enhance fluorescence for biological microscopy.

Finally, there were several references to the use of gold in contexts that were neither related to its surface chemistry or its optical properties. For example, gold has become a commonly used catalyst for growing nanorods of III-V semiconductors (eg. Alexandru Fachete and colleagues from the Australian National University (ANU)), while Jim Williams (ANU, Australia) used the ion implantation of Au to place nanocavities and nanoparticles into Si and SiO_2 coatings. Suresh Bhargava and colleagues (RMIT University, Australia) presented the results of work on co-precipitated Au-rare earth oxide catalysts. The useful properties of gold nanorods have already been noted, however the mechanism by which they form is not yet properly understood. The work of Gregory Grochola (RMIT, Australia) was therefore interesting since he had set up an atomistic model of their growth process, showing the effects of both surfactant and water molecules.

For me, the take-home message from this miscellany of gold-related items is that gold is an essential ingredient in modern science and technology, with uses and value out of proportion to its scarcity in the crust of this planet. In particular, I expect that gold will play a key role in many technologies currently under development. While individual applications may only use small quantities of the element, their aggregated effect is likely to have a material influence on overall consumption by the industrial sector.

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TOCAT 5: Fifth Tokyo Conference on Advanced Catalytic Science and Technology, Tokyo, Japan, 23-28 July 2006

The topics discussed at this international conference, having participants from over 40 countries, were wide ranging with plenary lectures on industrial catalysis, biotechnology, polymerization catalysis, methane reactions catalysed by supported metal clusters, and novel catalysts for organic synthesis. One of the most notable thoughts for the future is that fuels will increasingly come from biological sources and this will lead to requirements for new catalytic processes. There were five talks and ten posters on gold catalysis, and these presentations made relevant contributions to all these areas. The exhibition stand contributed by the World Gold Council (London, UK) and Project AuTEK (Randburg, South Africa) provided an effective centre for discussion of the many applications for gold summarized in a joint presentation during the conference (see below).

Highlights of Gold Presentations

Talks

1 Relations between homogeneous and heterogeneous gold catalysis – unique catalytic properties of gold for green chemistry, Avelino Corma, Universidad Politécnica de Valencia, Spain

Supported gold catalysts in which different amounts of Au^0, Au^+, and Au^{3+} are stabilized show different catalytic behaviour for chemoselective hydogenations, oxidations with air and carbon–carbon bond formation. Comparisons between trinuclear phosphine and Schiff base complexes of Au(I) and Au(III) provide a greater understanding of the nature of the active sites and the mechanisms, and have led to discovery of reactions uniquely catalysed by gold which cannot be achieved by any other noble metals.

2 Identification of the nature of the active form of gold in $Au/ZrCeO_4$ low temperature Water-Gas Shift catalysts, Christopher Hardacre, A Amieiro Foncesca, R Burch, Y Chen, J Fisher, A Goguet, P Hu, D Thompsett and D Tibiletti, Queen's University, Belfast and Johnson Matthey Technology Centre, Reading, UK

A combined experimental and theoretical investigation of the active form of gold in $Au/ZrCeO_4$ catalysts for the water-gas shift reaction was described. *In situ* EXAFS – XANES showed that the gold was in the form of dispersed gold ions in the fresh catalysts but that it is in the form of metallic clusters under water-gas shift conditions. The presence of Au-Ce distances in the EXAFS spectra and the fact that 15% of the gold can be re-oxidized, indicates close interaction with the support. DFT calculations further suggest that the active and stable gold is an $Au^{\delta+}$ species located at a cerium cation vacancy. It was concluded that metallic gold in close contact with the oxide support provides the active sites for the water-gas shift reaction on these very active catalysts.

3 Recent developments in the industrial application of gold catalysts, Christopher Corti, Richard Holliday, David Thompson and Elma van der Lingen, World Gold Council, London, UK and Project AuTEK, Mintek, South Africa

The use of gold and gold alloy catalysts in a range of commercially relevant reactions, processes and applications in air and water pollution control, fuel cells and chemical processing was summarized. The current status of research and development relating to these forthcoming uses was indicated, and recent developments described. These include a new hydrogen purification method, AuroPureH_2, based on room-temperature use of Au/TiO_2 and designed to remove carbon monoxide and prevent poisoning of the platinum catalysts used in fuel cells, and availability of 20kg quantities of gold catalysts suitable for use in development projects in industry. As the new science of gold catalysis advances, based on its unique catalytic activity and selectivity characteristics under very mild conditions, more commercially relevant applications will emerge.

4 Novel method for preparation of nanostructured Au/TiO_2 on SiO_2 support by colloidal synthesis, Anita Horvath, Andrea Beck, Antal Sárkány, Györgyi Stefler, Olga Geszt and László Guczi, Institute of Isotopes and Research Institute for Technical Physics and Materials Science, Budapest, Hungary

The formation of a gold/metal oxide interface is a key issue in the formation of active catalyst sites for carbon monoxide oxidation. The novel approach used here was to decrease the ratio of TiO_2 to gold by decoration of colloidal gold nanoparticles by TiO_2 moieties. The colloidal gold was prepared using a sol method to give uniformly sized particles, whilst the TiO_2 content was varied. The objective is to develop a modified sol gel preparation method that results in highly active Au/TiO_2 nanostructures supported on silica.

5 Performance control of hydrogenation catalysis by regulating the percentage of cationic gold in Au/ZrO_2 catalyst, Xin Zhang, Hui Shi and Bo-Qing Xu, Tsingua University, Beijing, China

Hydrogenation reactions of propene and 1,3-butadiene were studied over Au/ZrO_2 catalysts with various gold loadings. Activity and selectivity were correlated with the percentage of Au^{3+} present in the starting catalyst, but it seems unlikely that the oxidized gold would have survived the reducing conditions employed. However, competitive hydrogenation of 1,3-butadiene and propene in a propene-rich feed demonstrated that butadiene could be selectively hydrogenated using 0.76%Au/ZrO_2 catalyst. The removal of butadiene from olefin streams is important to prevent poisoning of industrial polymerization catalytic processes.

Posters

Amongst the industrial posters, the most exciting from an applications viewpoint was that presented by R Renneke, S McIntosh, V Arunajatesan, M Cruz, B Chen, T Tacke, H Lansink Rotgerink, A Geisselmann, R Mayer and M Stoyanova of Degussa on the development of higher performance vinyl acetate monomer catalysts based on supported Au-Pd in the presence of KOAc. Stable Au-Pd/KOAc catalysts with high durabilities have been used in well established industrial processes for the production of vinyl acetate since the 1970s. Other gold catalyst posters included 'Selective oxidation of propene over supported gold catalysts' by Z Suo, J Lu and L An (Yantai University and Dalian Institute of Chemical Physics, China), 'Modification of supported Au catalyst used for low temperature CO oxidation' by J Margitfalvi, M Hegedus, E Szabo, A Tompos, F Somodi and A Szegedi (Chemical Research Center, Hungary), 'Effects of TiO_2 crystal size on the catalytic activity of Au/TiO_2 for low temperature CO oxidation' by KL Yeung and KY Ho (The Hong Kong University of Science and Technology, Hong Kong) 'Poisoning effect of SO_2 on the catalytic activity of Au/TiO_2 investigated with XPS and *in situ* FTIR' by S Woo and MR Kim (Korea Institute of Advanced Industrial Science and Technology, South Korea), and aerial oxidation of cyclohexane to adipic acid using nano gold as catalyst in a solvent-free system' by RK Chaturvedi and S Senapati, National Chemical Laboratory, Pune, India.

The conference was well organized, and provided an excellent forum for discussion of new developments in catalysis, with special emphasis on those having industrial relevance.

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